SPECTROSCOPIC STUDY OF REDUCTION PRODUCTS OF AROMATIC SCHIFF BASES AND OF THEIR COPPER COMPLEXES

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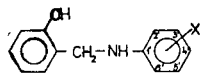
Secondary amines were prepared by the $NaBH_4$ reduction of salicylidene-anilines. The u.v. spectra of these amines, their complex-forming properties and the structures of their copper complexes are discussed.

It is well known that the C=N bond in all N-aryl-salicylaldimines is readily reduced by hydrogen in the presence of ADAMS's platinum catalyst [1, 2], to yield N-aryl-hydroxybenzylamines. A number of papers also deal with the reduction of Schiff bases with $NaBH_4$ under different conditions [*e.g.* 3]. The majority of Schiff bases were reduced in this way in accordance with the following equation:

$$R{-}CH{=}N{-}R' \xrightarrow[\text{methanol}]{NaBH_4} R{-}CH_2{-}NH{-}R'$$

where R=2-hydroxyphenyl and R'=3'- or 4'-substituted phenyl (Structure 1).



In the present paper we discuss the u.v. spectra of thirteen secondary amines obtained by the $NaBH_4$ reduction of salicylidene-anilines, and the visible spectra of their copper complexes.

Experimental

The secondary amines were prepared by portionwise addition of solid $NaBH_4$ (twice the molar amount of Schiff base) to a 5—10% methanolic solution of the corresponding parent base [3]. When the reaction became vigorous, the solution was cooled in ice. The mixture was refluxed for 10—15 min and the secondary amine was liberated by means of the addition of cold distilled water. Generally, no recrystallization was necessary. The yields were in the range 80—85%. The analytical data are listed in Table I. The copper salts were prepared by mixing an aqueous solution of

Table I

The secondary amines and their analytical data

No.	X	M.p.*	C%		H%	
			Calcd.	Found	Calcd.	Found
1	3'-CH_3	113.5—114.0	78.84	78.78	7.09	7.01
2	4'-CH_3	118.0—119.0		78.74		6.99
3	4'-C_2H_5	97.8—98.2	79.26	79.19	7.54	7.55
4	3'-OCH_3	67.0—67.5	73.34	73.27	6.59	6.50
5	4'-OCH_3	124.0—124.5		73.25		6.51
6	4'-OC_4H_9	92.0—92.5	75.24	75.18	7.86	7.85
7	H	109.0—109.2	78.37	78.33	6.61	6.60
8	2'-Cl	107.5—107.7	66.81	66.75	5.18	5.16
9	4'-Cl	122.0—122.2		66.74		5.09
10	3'-Br	118.0—118.4	55.13	55.09	4.35	4.30
11	4'-Br	127.5—127.7		55.10		4.27
12	3'-I	126.0—126.2	48.02	47.96	3.72	3.70
13	4'-I	129.7—129.8		47.91		3.66

* Uncorrected values.

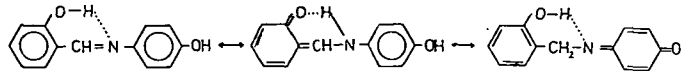
copper acetate monohydrate (0.01 mole) and a methanolic solution of the amine (0.01 mole). The deep-green solution which resulted slowly deposited green crystals on standing at room temperature. The isolated solids were recrystallized from methanol; their compositions were checked by Cu and C analysis (see Table III).

The u.v. and visible spectra were recorded at 298 K in spectroscopically pure solvents on a SPECORD UV-VIS spectrophotometer, using 1.0 and 0.1 cm quartz cells.

Results and Discussion

Rate of reduction. All the reduction processes were accompanied by a yellow → colourless change, which indicates that a reduction was taking place; by this means it was easy to follow the transformation spectrophotometrically. The reaction rate does not vary considerably with the nature of the substituents on the aniline ring; however, in general an electron-releasing group in the *p* position leads to a higher rate than for an electron-attracting group in this position.

The 4'-OH and 2'-OH derivatives show no change upon the addition of $NaBH_4$. This behaviour may be expected on the basis of tautomerization, which is well known for the salicylaldimines (Structure 2): the quinoid-type structure would be favoured



under the basic conditions of this reduction method. If such tautomerism occurs, the carbon atom of the C=N bond would be involved in a quinoid ring system and attack by $NaBH_4$ on this bond is highly improbable. If the OH group is located

Table II

U.v. spectral data on amines (nm and log ε)

No.	In methanol				In basic media			In acidic media		
1	207	250	~280	~305	210	243	294	203	~210	276
	(4.62)	(4.05)			(4.57)	(4.34)	(3.85)	(4.44)		(3.59)
2	203	244	~277	~300	210	243	293	203	~215	278
	(4.67)	(4.14)			(4.51)	(4.40)	(3.87)	(4.41)		(3.59)
3	203	246	~280	~310	209	243	294	202	~215	279
	(4.86)	(4.36)			(4.41)	(4.31)	(3.75)	(4.41)		(3.56)
4	212	248	281	~300	213	243	293	203	221	277
	(4.56)	(3.98)	(3.58)		(4.60)	(4.31)	(3.91)	(4.53)	(4.28)	(3.80)
5	203	241	~276	304	209	241	294	202	224	278
	(4.22)	(4.15)		(3.22)	(4.28)	(4.33)	(3.78)	(4.40)	(4.28)	(3.71)
6	202	242	~276	306	209	242	294	202	225	277
	(4.65)	(4.55)		(3.29)	(4.30)	(4.37)	(3.82)	(4.46)	(4.30)	(3.71)
7	205	246	276	~310	209	243	294	203	~220	280
	(4.50)	(4.16)	(3.63)		(4.33)	(4.33)	(3.82)	(4.47)		(3.52)
8	209	253	~275	302	212	250	294	202	~215	279
	(4.75)	(4.26)		(3.42)	(4.53)	(4.27)	(3.83)	(4.46)		(3.52)
9	206	256	—	307	209	252	294	202	218	280
	(4.19)	(3.98)		(3.21)	(4.34)	(4.27)	(3.79)	(4.41)	(4.24)	(3.47)
10	212	253	~280	303	213	248	294	203	~220	280
	(4.65)	(4.23)		(3.36)	(4.54)	(4.27)	(3.86)	(4.52)		(3.50)
11	205	256	—	307	209	257	293	202	221	279
	(4.56)	(4.35)		(3.23)	(4.30)	(4.24)	(3.77)	(4.51)	(4.24)	(3.54)
12	220	254	~280	304	221	253	295	203	~230	279
	(4.66)	(4.25)		(3.40)	(4.22)	(3.89)	(3.51)	(4.17)		(3.22)
13	203	—	260	308	209	262	294	202	237	279
	(4.70)		(4.55)		(4.30)	(4.35)	(3.82)	(4.53)	(4.21)	(3.59)

at the 3' position, there is no opportunity for such a quinoidal structure to exist; hence, reduction is to be expected in this case.

U.v. spectra of amines. The nm and log ε data on the characteristic bands of the amines are listed in Table II.

The u.v. spectra of structurally analogous amines are quite similar, two bands of high intensity appearing at around 203—220 and 240—260 nm (Figs. 1—4). On the long-wave side of the second band, two medium-intensity inflexions can be found. The two main bands are assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic nucleus. The energy and intensity of the 240—260 nm band vary approximately in accordance with the HAMMETT σ_p constants. The asymmetry of this band indicates the overlapping of the bands of the aldehyde and amine components.

In alkaline media there are three bands, in the ranges 208—222, 240—260 and 290—295 nm, and the intensities of the bands change to only a small extent. In acidic solution all the amines have two characteristic bands, at 202—203 and 276—280 nm, while a shoulder appears at about 210—230 nm (Figs. 1—4).

Copper (II) complexes. The N-phenyl-*o*-hydroxybenzyl-amines form complexes with copper ions; however, in contrast with the parent Schiff bases, they do not react with other transition metal ions. No reaction can be observed between copper ions and amines bearing *ortho* substituents on the phenyl ring. The general formula of the metal salts is CuLAc; the complexes studied are listed in Table III.

The complexes have anomalously low magnetic moments; the B.M. values lie in the range 1.3—1.4. No correlation can be found between the B.M. values and the nature of the substituents on the aniline ring. It is known from structure determination [4] that copper acetate monohydrate is a binuclear molecule with two square-

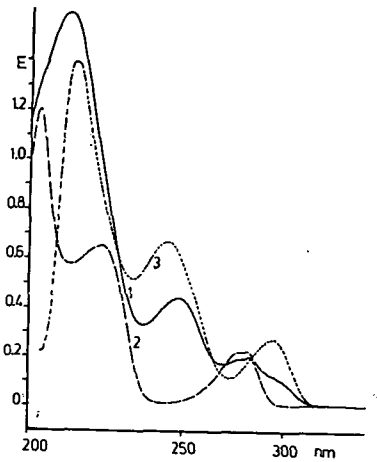


Fig. 1. U.v. spectra of $3.78 \cdot 10^{-4}$ mol/dm³ N-(*m*-methoxyphenyl)-*o*-hydroxybenzylamine in 1: methanol; 2: 0.1 mol/dm³ H_2SO_4/CH_3OH; 3: 0.1 mol/dm³ $NaOH/CH_3OH$. d = 0.1 cm

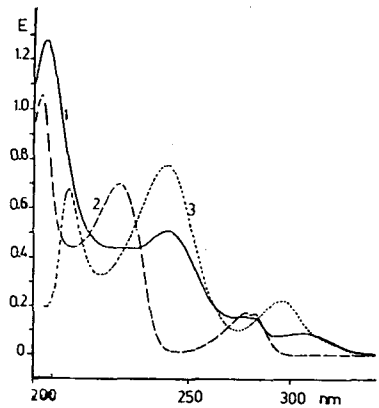


Fig. 2. U.v. spectra of $3.5 \cdot 10^{-4}$ mol/dm³ N-(*p*-methoxyphenyl)-*o*-hydroxybenzylamine in 1: methanol; 2: 0.1 mol/dm³ H_2SO_4/CH_3OH; 3: 0.1 mol/dm³ $NaOH/CH_3OH$. d = 0.1 cm

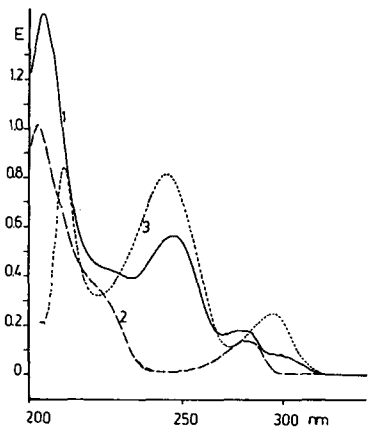


Fig. 3. U.v. spectra of $4.36 \cdot 10^{-4}$ mol/dm³ N-phenyl-*o*-hydroxybenzylamine in 1: methanol; 2: 0.1 mol/dm³ H_2SO_4/CH_3OH; 3: 0.1 mol/dm³ $NaOH/CH_3OH$. d = 0.1 cm

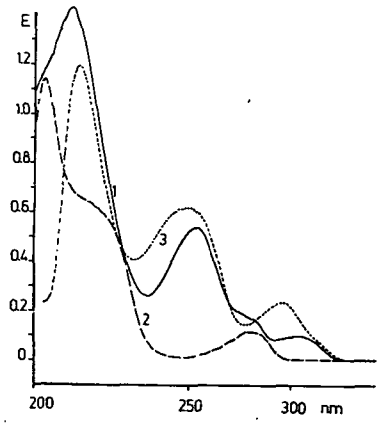


Fig. 4. U.v. spectra of $3.22 \cdot 10^{-4}$ mol/dm³ N-(*m*-bromophenyl)-*o*-hydroxybenzylamine in 1: methanol; 2: 0.1 mol/dm³ H_2SO_4/CH_3OH; 3: 0.1 mol/dm³ $NaOH/CH_3OH$. d = 0.1 cm

Table III

Analytical and spectral data on $[CuLAc]_2$ *type complexes*

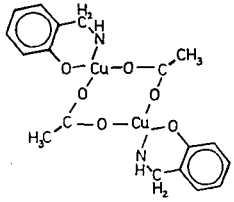
Aniline ring subst.	C%		Cu%		nm and log ε*
	Calcd.	Found	Calcd.	Found	
4'-OC_4H_9	58.1	57.9	16.2	16.2	666(2.03)
4'-OCH_3	54.8	54.7	18.1	17.9	670(1.98)
4'-CH_3	57.4	57.2	19.0	19.1	680(2.00)
4'-C_2H_5	58.5	58.5	18.2	18.1	682(1.98)
H	56.2	56.0	19.8	19.7	686(1.83)
4'-Cl	50.7	50.6	17.9	17.8	692(1.74)
4'-Br	45.1	45.0	15.9	15.7	700(1.60)

* In methanol.

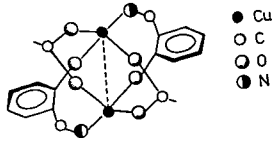
pyramidal CuO_5 groups (the one-electron orbital ground state is $d_{x^2-y^2}$); the Cu-Cu distance is 2.64 Å. The anomalously low paramagnetism (1.4 B.M.) and the temperature variation of the magnetic susceptibility [5] indicate a binuclear structure and the existence of a weak covalent copper-copper bond in the crystalline state and in organic solvents, too. Taking our B.M. values into consideration, it is very likely that the copper compounds studied similarly have a binuclear structure and that their real formula is $[CuLAc]_2$.

The visible spectra of methanolic solutions of the complexes are quite similar. Only one broad band can be found, at around 660—690 nm, which is assigned to the $d_{z^2} \leftarrow d_{x^2-y^2}$ transition (Table III). The intensity of the band corresponds to that of the d-d band characteristic for $3d^9$ systems in a strong ligand field. The energy and intensity of the bands decrease with the HAMMETT σ_p constants.

We assume that the copper compounds may have one of two alternative structures. In Structure 3 the Schiff base behaves as a bidentate ligand to one copper ion,



while in Structure 4 one Schiff base ligand is bound to two copper ions. In our opi-



nion the latter structure is not likely because of stereochemical difficulties.

In the range 360—380 nm the solution spectra show a sharp inflexion, which is assumed to be closely related to the copper-copper interaction. This is borne out by

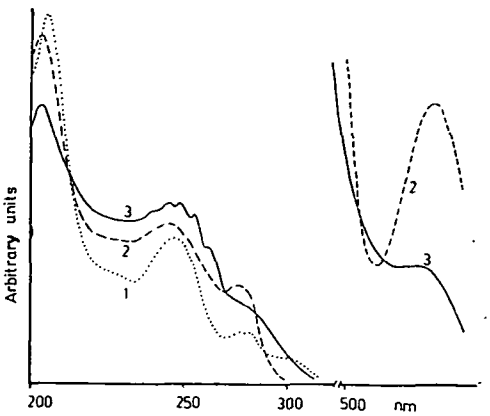


Fig. 5. Spectra of methanolic solutions of 1: N-phenyl-*o*-hydroxybenzylamine; 2: $[CuLAc]_2$; 3: product obtained from pyridine solution of $[CuLAc]_2$ after three days

the solvent effect upon these absorption bands, similarly as found by YAMADA ET AL. [6] in connection with the copper salts of monocarboxylic fatty acids.

The i.r. spectra measured in KBr discs show bands at about 1580 and 1600 cm^{-1}, while sodium acetate, which contains the carboxylate in an ionized form, gives a broad and a sharp band at around 1560 cm^{-1}. This difference indicates that the state of the carboxylate ion in our complexes differs from that in sodium acetate.

The pyridine solutions of the complexes show spectra with similar structure as for those in methanolic solution; the single band appears in the vicinity of 670 nm. In time the deep-green solutions turn brown and naturally the spectra change, too. The 670 nm band disappears and only a broad inflexion remains (Fig. 5). In the u.v. region the spectral features of the secondary amines and their copper complexes are totally similar. The products obtained from pyridine solutions of the $[CuLAc]_2$ complexes show a band at around 240—260 nm, with vibronic structure indicating bonding of the pyridine molecule. Studies on the described transformation are in progress.

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СПЕКТРОСКОПИЧЕСКОЕ ИЗУЧЕНИЕ ПРОДУКТОВ ВОССТАНОВЛЕНИЯ АРОМАТИЧЕСКИХ ОСНОВАНИЙ ШИФФА И ИХ МЕДНЫХ КОМПЛЕКСОВ

Й. Часар

Приготовлены вторичные амины восстановлением салицилиден-анилинов с помощью $NaBH_4$. Обсуждены УФ спектры аминов и их комплексо образующие свойства, рассмотрены структуры медных комплексов.